

DECLARATION

I, Kenshi Uchida, a national of Japan, c/o Sumitomo Chemical Intellectual Property Service, Limited, 5-33, Kitahama 4-chome, Chuo-ku, Osaka 541-8550, Japan, declare that to the best of my knowledge and belief the attached in a full, true, and faithful translation into English made by me of the priority document, Japanese Patent Application No. 2000-371180.

Signed this 24 th day of August, 2009

Kenshi Uchida

Kenshi UCHIDA

PATENT OFFICE
JAPANESE GOVERNMENT

This is to certify that the annexed is a true copy of the following application
as filed with this office.

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Applicant(s): Sumitomo Chemical Company, Limited

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| [Inventor] | |
| [Address] | c/o Sumitomo Chemical Company, limited, 6, Kitahara, Tsukuba-shi, Ibaraki |
| [Name] | Shuji DOI |
| [Inventor] | |
| [Address] | c/o Sumitomo Chemical Company, limited, 6, Kitahara, Tsukuba-shi, Ibaraki |
| [Name] | Yoshiaki TSUBATA |
| [Inventor] | |
| [Address] | c/o Sumitomo Chemical Company, limited, 6, Kitahara, Tsukuba-shi, Ibaraki |
| [Name] | Takahiro UEOKA |
| [Applicant] | |
| [Identification No.] | 000002093 |
| [Name] | Sumitomo Chemical Company, Limited |
| [Patent Attorney] | |
| [Identification No.] | 100093285 |
| [Name] | Takashi KUBOYAMA |
| [Telephone No.] | 06-220-3405 |
| [Elected Patent Attorney] | |
| [Identification No.] | 100094477 |
| [Name] | Naoyoshi JINNO |
| [Telephone No.] | 06-220-3405 |
| [Elected Patent Attorney] | |
| [Identification No.] | 100113000 |
| [Name] | Tohru NAKAYAMA |
| [Telephone No.] | 06-220-3405 |
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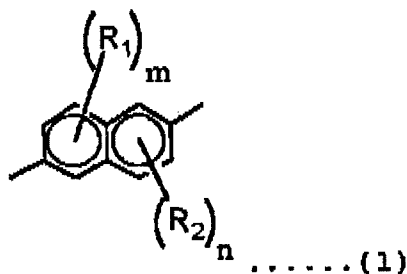
[NAME OF DOCUMENT] SPECIFICATION

[TITLE OF THE INVENTION] POLYMERIC FLUORESCENT SUBSTANCE AND
POLYMER LIGHT-EMITTING DEVICE USING THE SAME

[SCOPE OF CLAIMS FOR PATENT]

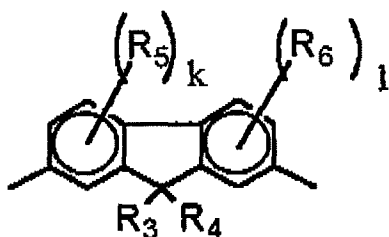
[Claim 1]

A polymeric fluorescent substance exhibiting fluorescence in the solid state, having a polystyrene reduced number-average molecular weight of 10^3 to 10^8 , and containing one or more repeating units of formula (1) and one or more repeating units of formula (2),



[in the formula, R_1 and R_2 represent each independently a group selected from the group consisting of alkyl group, alkoxy group, alkylthio group, alkylsilyl group, alkylamino group, aryl group, aryloxy group, arylsilyl group, arylamino group, arylalkyl group, arylalkoxy group, arylalkylsilyl group, arylalkylamino group, arylalkenyl group, arylalkynyl group, monovalent heterocyclic compound group, and cyano group; m and n are integers of 0-3 each independently; however, m and n are not 0 at the same time; when m is two or more, two or more R_1 may be the same or different; when n is two or more, the plurality

of R_2 may be the same or different; moreover, R_1 and R_2 may be connected to form a ring; furthermore, when R_1 and R_2 contain an alkyl chain, said alkyl chain may be interrupted by a group containing a hetero atom]



.....(2)

[in the formula, R_3 and R_4 represent independently a group selected from the group consisting of a hydrogen atom, alkyl group, aryl group, and a heterocyclic compound group; R_5 and R_6 show each independently a group selected from the group consisting of alkyl group, alkoxy group, alkylthio group, alkylsilyl group, alkylamino group, aryl group, aryloxy group, arylsilyl group, arylamino group, arylalkyl group, arylalkoxy group, arylalkylsilyl group, arylalkylamino group, arylalkenyl group, arylalkynyl group, monovalent heterocyclic compound group, and cyano group; k and l are integers of 0-3 each independently; when k is two or more, the plurality of R_5 may be the same or different; when l is two or more, the plurality of R_6 may be the same or different; $R_3 - R_6$ may be connected to form a ring; furthermore, in the case of the group in which $R_3 - R_6$ contains an alkyl chain, this alkyl chain may be interrupted by a group containing a hetero atom].

[Claim 2]

The polymeric fluorescent substance according to Claim 1, wherein the total amount of repeating units represented by formulae (1) and (2) is 50 mol% or more based on the total amount of all repeating units, and the amount of repeating units represented by the formula (1) is 0.1 mol% or more and 50 mol% or less based on the total amount of the repeating units represented by the formulae (1) and (2).

[Claim 3]

A polymer light emitting device comprising at least a light emitting layer between a pair of electrodes composed of an anode and a cathode at least one of which is transparent or semi-transparent wherein the light emitting layer contains a polymeric fluorescent substance according to Claim 1 or 2.

[Claim 4]

The polymer light emitting device according to Claim 3, further comprising a layer containing an conducting polymer disposed between one electrode and the light emitting layer so that the layer containing an conducting polymer is adjacent to said electrode.

[Claim 5]

The polymer light emitting device according to Claim 3, further comprising an insulation layer having a thickness of 2 nm or less disposed between one electrode and the light emitting

layer so that the insulation layer is adjacent to said electrode.

[Claim 6]

The polymer light emitting device according to any one of Claims 3 to 5, further comprising a layer comprising an electron transporting compound disposed between the cathode and the light emitting layer so that the layer comprising an electron transporting compound is adjacent to said light emitting layer.

[Claim 7]

The polymer light emitting device according to any one of Claims 3 to 5, further comprising a layer comprising a hole transporting compound disposed between the anode and the light emitting layer so that the layer comprising a hole transporting compound is adjacent to said light emitting layer.

[Claim 8]

The polymer light emitting device according to any one of Claims 3 to 5, further comprising a layer comprising an electron transporting compound and a layer comprising a hole transporting compound disposed between the cathode and the light emitting layer so that the layer comprising an electron transporting compound is adjacent to said light emitting layer, and the layer comprising a hole transporting compound is adjacent to said light emitting layer.

[Claim 9]

A flat light source obtained by using the polymer light emitting device according to any one of Claims 3 to 8.

[Claim 10]

A segment display obtained by using the polymer light emitting device according to any one of Claims 3 to 8.

[Claim 11]

A dot matrix display obtained by using the polymer light emitting device according to any one of Claims 3 to 8.

[Claim 12]

A liquid crystal display obtained by using the polymer light emitting device according to any one of Claims 3 to 8 as a back-light.

[DETAILED DESCRIPTION OF THE INVENTION]

[0001]

[Field of the Invention]

The present invention relates to a polymeric fluorescent substance and more specifically a polymer light-emitting device (hereinafter, may be referred to as polymer LED) using the same.

[0002]

[Prior Art]

Differing from low molecular weight materials, light emitting materials having higher molecular weight (polymeric fluorescent substances) have a merit that they can be dissolved in a solvent, and can form a light emitting layer by a coating method, and various substances have been studied. For example, J. Mater. Sci. Mater. Ele., 11, p. 111 (2000) describes

polymers containing unsubstituted naphthalene and fluorene.

[0003]

[Problems to be Solved by the Invention]

An object of the present invention is to provide a polymer LED of high performance which can be driven at lower voltage with high efficiency, using a polymeric fluorescent substance comprising a fluorene and a naphthalene, which manifests strong fluorescence.

[0004]

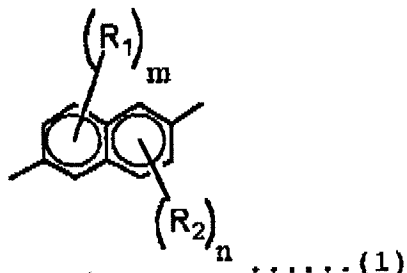
[Means for Solving the Problem]

The present inventors have intensively studied in view of the above problems, and resultantly found that a polymeric fluorescent substance exhibiting fluorescence in the solid state, having a polystyrene reduced number-average molecular weight of 10^3 to 10^8 , and comprising 2,6-naphthalene having a substituent and a fluorene, shows strong fluorescence, and a polymer LED of high performance which can be driven at lower voltage with high efficiency can be obtained using the above-mentioned polymeric fluorescent substance, leading to completion of the invention.

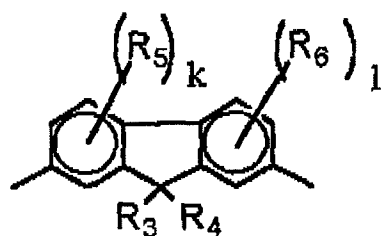
[0005]

Namely, the present invention relates to [1] a polymeric fluorescent substance exhibiting fluorescence in the solid state, having a polystyrene reduced number-average molecular weight of 10^3 to 10^8 , and containing one or more repeating units

of formula (1) and one or more repeating units of formula (2),



[in the formula, R_1 and R_2 represent each independently a group selected from the group consisting of alkyl group, alkoxy group, alkylthio group, alkylsilyl group, alkylamino group, aryl group, aryloxy group, arylsilyl group, arylamino group, arylalkyl group, arylalkoxy group, arylalkylsilyl group, arylalkylamino group, arylalkenyl group, arylalkynyl group, monovalent heterocyclic compound group, and cyano group; m and n are integers of 0-3 each independently; however, m and n are not 0 at the same time; when m is two or more, two or more R_1 may be the same or different; when n is two or more, the plurality of R_2 may be the same or different; moreover, R_1 and R_2 may be connected to form a ring; furthermore, when R_1 and R_2 contain an alkyl chain, said alkyl chain may be interrupted by a group containing a hetero atom]



.....(2)

[in the formula, R_3 and R_4 represent independently a group selected from the group consisting of a hydrogen atom, alkyl group, aryl group, and a heterocyclic compound group; R_5 and R_6 show each independently a group selected from the group consisting of alkyl group, alkoxy group, alkylthio group, alkylsilyl group, alkylamino group, aryl group, aryloxy group, arylsilyl group, arylamino group, arylalkyl group, arylalkoxy group, arylalkylsilyl group, arylalkylamino group, arylalkenyl group, arylalkynyl group, monovalent heterocyclic compound group, and cyano group; k and l are integers of 0-3 each independently; when k is two or more, the plurality of R_5 may be the same or different; when l is two or more, the plurality of R_6 may be the same or different; $R_3 - R_6$ may be connected to form a ring; furthermore, in the case of the group in which $R_3 - R_6$ contains an alkyl chain, this alkyl chain may be interrupted by a group containing a hetero atom].

[0006]

Moreover, the present invention relates to [2] a polymer light emitting device comprising at least a light emitting layer

between a pair of electrodes composed of an anode and a cathode at least one of which is transparent or semi-transparent wherein the light emitting layer contains a polymeric fluorescent substance according to [1]. Further, the present invention relates to [3] a flat light source obtained by using the above polymer light emitting device of [2]. Still further, the present invention relates to [4] a segment display obtained by using the above polymer light emitting device of [2]. Further, the present invention relates to [5] a dot matrix display obtained by using the above polymer light emitting device of [2]. Further, the present invention relates to [6] a liquid crystal display obtained by using the above polymer light emitting device of [2] as a back-light.

[0007]

[Modes for Carrying out the Invention]

[0008]

The polymeric fluorescent substance of the present invention exhibits fluorescence in the solid state, has a polystyrene reduced number-average molecular weight of 10^3 to 10^6 , and contains one or more repeating units of the above formula (1) and one or more repeating units of the above formula (2).

The total amount of repeating units represented by formulae (1) and (2) is preferably 50 mol% or more based on the total amount of all repeating units. The amount of repeating units represented by the formula (1) is preferably 0.1 mol% or more

and 50 mol% or less based on the total amount of the repeating units represented by the formulae (1) and (2). More preferably, the total amount of repeating units represented by formulae (1) and (2) is 50 mol% or more based on the total amount of all repeating units, and the amount of repeating units represented by the formula (1) is preferably 0.1 mol% or more and 50 mol% or less based on the total amount of the repeating units represented by the formulae (1) and (2).

[0009]

The repeating unit represented by the above formula (1) is a 2,6-naphthalene having a substituent. The repeating unit represented by the above formula (2) is a fluorene group which may have a substituent. R_1 and R_2 in formula (1), and R_5 and R_6 in formula (2) independently represents a group selected from alkyl group, alkoxy group, alkylthio group, alkylsilyl group, alkylamino group, aryl group, aryloxy group, arylsilyl group, arylamino group, arylalkyl group, arylalkoxy group, arylalkylsilyl group, arylalkylamino group, arylalkenyl group, aryl alkynyl group, heterocyclic compound group, and cyano group.

[0010]

Cases where R_1 , R_2 , R_5 , and R_6 are other than cyano groups are explained as follows.

The alkyl group may be linear, branching or cyclic, and has usually about one to 20 carbon atoms. Examples thereof

include specifically methyl group, ethyl group, propyl group, i-propyl group, butyl group, i-butyl group, t-butyl group, pentyl group, hexyl group, cyclohexyl group, heptyl group, octyl group, 2-ethylhexyl group, nonyl group, decyl group, 3,7-dimethyloctyl group, lauryl group, etc. Among them, pentyl group, hexyl group, octyl group, 2-ethylhexyl group, decyl group, and 3,7- dimethyl octyl group are preferable.

[0011]

The alkoxy group may be linear, branching or cyclic, and has usually about one to 20 carbon atoms.

Examples thereof include specifically methoxy group, ethoxy group, propyloxy group, i-propyloxy group, butoxy group, 1-butoxy group, t-butoxy group, pentyloxy group, hexyloxy group, cyclohexyloxy group, heptyloxy group, octyloxy group, 2-ethylhexyloxy group, nonyloxy group, decyloxy group, 3,7-dimethyloctyloxy group, lauryloxy group etc. Among them, pentyloxy group, hexyloxy group, octyloxy group, 2-ethylhexyloxy group, decyloxy group, and 3,7- dimethyl octyloxy group are preferable.

[0012]

The alkoxy group may be linear, branching or cyclic, and has usually about one to 20 carbon atoms. Examples thereof include specifically methylthio group, ethylthio group, propylthio group, and i-propylthio group, butylthio group, i-butylthio group, t-butylthio group, pentylthio group,

hexylthio group, cyclo hexylthio group, heptylthio group, octylthio group, 2-ethylhexylthio group, nonylthio group, decylthio group, 3,7-dimethyloctylthio group, laurylthio group etc. Among them, pentylthio group, hexylthio group, octylthio group, 2-ethylhexylthio group, decylthio group, and 3,7-dimethyloctylthio group are preferable.

[0013]

The alkylsilyl group may be linear, branching or cyclic, and has usually about one to 60 carbon atoms. Examples thereof include specifically methylsilyl group, ethylsilyl group, propylsilyl group, and 1-propylsilyl group, butylsilyl group, i-butylsilyl group, t-butylsilyl group, pentylsilyl group, hexylsilyl group, cyclohexylsilyl group, heptylsilyl group, octylsilyl group, 2-ethylhexylsilyl group, nonylsilyl group, decylsilyl group, 3,7-dimethyloctylsilyl group, laurylsilyl group, trimethylsilyl group, ethyldimethylsilyl group, propyldimethylsilyl group, 1-propyldimethylsilyl group, butyldimethylsilyl group, t-butyldimethylsilyl group, pentyldimethylsilyl group, hexyldimethylsilyl group, heptyldimethylsilyl group, octyldimethylsilyl group, 2-ethylhexyldimethylsilyl group, nonyldimethylsilyl group, decyldimethylsilyl group, 3,7-dimethyloctyl-dimethylsilyl group, lauryldimethylsilyl group, etc. Among them, pentylsilyl group, hexylsilyl group, octylsilyl group, 2-ethylhexylsilyl group, decylsilyl group, 3,7-dimethyloctylsilyl group,

pentyldimethylsilyl group, hexyldimethylsilyl group, octyldimethylsilyl group, 2-ethylhexyl-dimethylsilyl group, decyldimethylsilyl group, 3,7-dimethyloctyl-dimethylsilyl group are preferable.

[0014]

The alkylamino group may be linear, branching or cyclic, and has usually about one to 40 carbon atoms. Either monoalkylamino group or dialkylamino group may be available. Examples thereof include specifically methylamino group, dimethylamino group, ethylamino group, diethylamino group, propylamino group, i-propylamino group, butylamino group, i-butylamino group, t-butylamino group, pentylamino group, hexylamino group, cyclohexylamino group, heptylamino group, octylamino group, 2-ethylhexylamino group, nonylamino group, decylamino group, 3,7-dimethyloctylamino group, laurylamino group, etc. Among them, pentylamino group, hexylamino group, octylamino group, 2-ethylhexylamino group, decylamino group, and 3,7-dimethyloctylamino group are preferable.

[0015]

The aryl group has usually about 6 to 60 carbon atoms. Examples thereof include phenyl group, C₁₋₁₂ alkoxyphenyl group (C₁₋₁₂ means that the number of carbon atoms is from 1 to 12), C₁₋₁₂ alkylphenyl group, 1-naphtyl group, 2-naphtyl group, etc. Among them, C₁₋₁₂ alkoxyphenyl group, and C₁₋₁₂ alkylphenyl group are preferable.

[0016]

The aryloxy group has usually about 6 to 60 carbon atoms. Examples thereof include specifically, phenoxy group, C₁₋₁₂ alkoxyphenoxy group, C₁₋₁₂ alkylphenoxy group, 1-naphtyloxy group, 2-naphtyloxy group, etc. Among them, C₁₋₁₂ alkoxyphenoxy group, and C₁₋₁₂ alkylphenoxy group are preferable.

[0017]

The arylsilyl group has usually about 6 to 60 carbon atoms. Examples thereof include specifically, phenylsilyl group, C₁₋₁₂ alkoxyphenylsilyl group, C₁₋₁₂ alkylphenylsilyl group, 1-naphtylsilyl group, 2-naphtylsilyl group, dimethylphenylsilyl group, etc. Among them, C₁₋₁₂ alkoxyphenylsilyl group and C₁₋₁₂ alkylphenylsilyl group are preferable.

[0018]

The arylamino group has usually about 6 to 60 carbon atoms. Examples thereof include specifically, diphenylamino group, C₁₋₁₂ alkoxyphenylamino group, di(C₁₋₁₂ alkoxyphenyl)amino group, di(C₁₋₁₂ alkylphenyl)amino group, 1-naphtylamino group, 2-naphtylamino group, etc. Among them C₁₋₁₂ alkylphenylamino group, and di(C₁₋₁₂ alkylphenyl)amino group are preferable.

[0019]

The arylalkyl group has usually about 7 to 60 carbon atoms. Examples thereof include specifically, phenyl-C₁₋₁₂alkyl group, C₁₋₁₂alkoxyphenyl-C₁₋₁₂alkyl group, C₁₋₁₂ alkylphenyl-C₁₋₁₂alkyl

group, 1-naphtyl- C_{1-12} alkyl group, 2-naphtyl- C_{1-12} alkyl group, etc. Among them, C_{1-12} alkoxyphenyl- C_{1-12} alkyl group, and C_{1-12} alkylphenyl- C_{1-12} alkyl group are preferable.

[0020]

The arylalkoxy group has usually about 7 to 60 carbon atoms. Examples thereof include specifically, phenyl- C_{1-12} alkoxy group, C_{1-12} alkoxyphenyl- C_{1-12} alkoxy group, C_{1-12} alkylphenyl- C_{1-12} alkoxy group, 1-naphtyl- C_{1-12} alkoxy group, 2-naphtyl- C_{1-12} alkoxy group, etc. Among them, C_{1-12} alkoxyphenyl- C_{1-12} alkoxy group, and C_{1-12} alkylphenyl- C_{1-12} alkoxy group are preferable.

[0021]

The arylalkylsilyl group has usually about 7 to 60 carbon atoms. Examples thereof include specifically, phenyl- C_{1-12} alkylsilyl group, C_{1-12} alkoxyphenyl- C_{1-12} alkylsilyl group, C_{1-12} alkylphenyl- C_{1-12} alkylsilyl group, 1-naphtyl- C_{1-12} alkylsilyl group, 2-naphtyl- C_{1-12} alkylsilyl group, phenyl- C_{1-12} alkyldimethylsilyl group, etc. Among them, C_{1-12} alkoxyphenyl- C_{1-12} alkylsilyl group, and C_{1-12} alkylphenyl- C_{1-12} alkylsilyl group are preferable.

[0022]

The arylalkylamino group has usually about 7 to 60 carbon atoms. Examples thereof include specifically, phenyl- C_{1-12} alkylamino group, C_{1-12} alkoxyphenyl- C_{1-12} alkylamino group, C_{1-12} alkylphenyl- C_{1-12} alkylamino group, di(C_{1-12} alkoxyphenyl- C_{1-12} alkyl)amino group, di(C_{1-12} alkylphenyl- C_{1-12} alkyl)amino

group, 1-naphtyl- C_{1-12} alkylamino group, 2-naphtyl- C_{1-12} alkylamino group, etc. Among them, C_{1-12} alkylphenyl- C_{1-12} alkylamino group, and di(C_{1-12} alkylphenyl- C_{1-12} alkyl)amino group are preferable.

[0023]

The heterocyclic compound group has usually about 4 to 60 carbon atoms. Examples thereof include thienyl group, C_{1-12} alkylthienyl group, pyroryl group, furyl group, pyridyl group, C_{1-12} alkylpyridyl group, etc. Among them, thienyl group, C_{1-12} alkylthienyl group, pyridyl group, and C_{1-12} alkylpyridyl group are preferable.

[0024]

In the above formula (2), R_3 and R_4 independently represents a group selected from a hydrogen atom, an alkyl group, an aryl group, and a heterocyclic compound group.

[0025]

In the case where R_3 and R_4 are substituents other than a hydrogen atom or a cyano group, the alkyl group may be linear, branching or cyclic, and has usually about one to 20 carbon atoms. Examples thereof include specifically methyl group, ethyl group, propyl group, butyl group, pentyl group, hexyl group, heptyl group, octyl group, nonyl group, decyl group, lauryl group, etc. Among them, methyl group, ethyl group, pentyl group, hexyl group, heptyl group, and an octyl group are preferable.

[0026]

The aryl group has usually about 6 to 60 carbon atoms. Examples thereof include specifically phenyl group, C₁₋₁₂ alkoxyphenyl group, C₁₋₁₂alkylphenyl group, 1-naphtyl group, 2-naphtyl group, etc. Among them, phenyl group and C₁₋₁₂ alkylphenyl group are preferable.

[0027]

The heterocyclic compound group has usually about 4 to 60 carbon atoms. Examples thereof include specifically thienyl group, C₁₋₁₂ alkylthienyl group, pyroryl group, furyl group, pyridyl group, C₁₋₁₂ alkylpyridyl group, etc. Among them, thienyl group, C₁₋₁₂ alkylthienyl group, pyridyl group, and C₁₋₁₂ alkylpyridyl group are preferable.

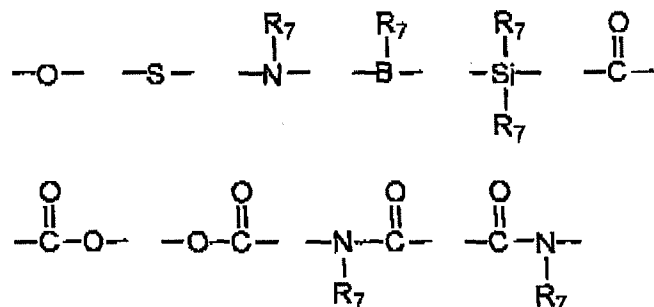
The symbols m and n are integers of 0-3 each independently; however, m and n are not 0 at the same time; the repeating unit represented by formula (1) contains at least one substituent; the symbols k and l are integers of 0-3 each independently.

In the repeating unit represented by formula (1), when m is two or more, a plurality of R₁s may be the same or different; when n is two or more, a plurality of R₂s may be the same or different; moreover, R₁ and R₂ may be connected to form a ring; furthermore, when R₁ and R₂ contain an alkyl chain, said alkyl chain may be interrupted by a group containing a hetero atom.

In the repeating unit represented formula (2), when k is

two or more, the plurality of R_5 s may be the same or different; when 1 is two or more, the plurality of R_6 s may be the same or different; $R_3 - R_6$ may be connected to form a ring; furthermore, in the case of the group in which $R_3 - R_6$ contains an alkyl chain, this alkyl chain may be interrupted by a group containing a hetero atom. Examples of the heteroatom include following groups.

[0028]



Here, R_7 include a hydrogen atom, an alkyl group having 1-20 carbon atoms, an aryl group having 6-60 carbon atoms, and a heterocyclic compound group having 4-60 carbon atoms.

[0029]

In the substituents containing an alkyl chain, said alkyl chain may be linear, branching or cyclic. Combination thereof may be also included. When the alkyl chain is not linear, examples thereof include iso-amyl group, 2-ethylhexyl group, 3,7-dimethyloctyl group, cyclohexyl group, 4- C_{1-12} alkylcyclohexyl group, etc.

In order to improve the solubility of a polymeric fluorescent

substance in a solvent, it is suitable that at least one substituent of the above formula (1) contains an alkyl chain having cyclic or branching structure.

In order to obtain a material having strong fluorescence, it is suitable that the repeating unit including substituents has less symmetry. Moreover, among the examples of R_1 - R_6 , when it includes an alkyl group or a heterocyclic compound group as a part of the structure, they may have further one or more substituents.

[0030]

Further, a protecting group may be used to stabilize the terminal group of a polymeric fluorescent substance in accordance with the present invention since if an active polymerizable group remains intact, there is a possibility of reduction of the light emitting property and life of the polymeric fluorescent substance when the material is used in a device.

Examples thereof include structures containing a bond to an aryl group or a heterocyclic compound group via a vinylene group. Specifically, protecting groups described in JP-A No. 9-45478, chemical formula 10, and the like are exemplified.

[0031]

As for a method of the polymeric fluorescent substances, there are exemplified a method in which polymerization is

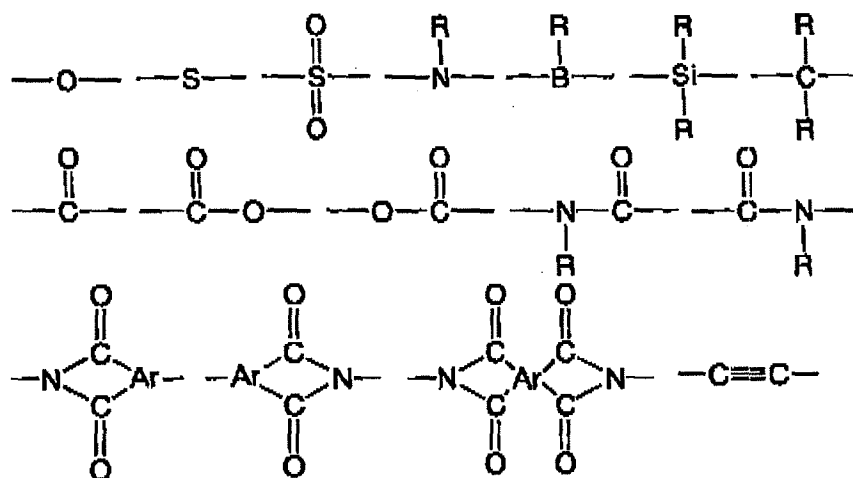
effected according to a Suzuki coupling reaction from the corresponding monomer, a method in which polymerization is effected according to a Grignard reaction, a method in which polymerization is effected using a Ni(0) catalyst, a method in which polymerization is effected using an oxidizing agent such as FeCl₃ and the like, a method of effecting oxidation polymerization electrochemically, a method according to decomposition of an intermediate polymer having a suitable releasing group, and the like. Of them, the method of effecting polymerization according to a Suzuki coupling reaction, the method of effecting polymerization according to a Grignard reaction, the method of effecting polymerization using a Ni(0) catalyst are preferable since reaction control is easy.

[0032]

The polymeric fluorescent substance may contain a repeating unit other than repeating units represented by the formula (1) or (2), in an amount which does not deteriorate fluorescent property and charge carrying property. Further, repeating units represented by the formula (1) or (2) and other repeating units may be connected with a non-conjugation unit, or such a non-conjugation part may be contained in the repeating unit. As the bonding structure, there are exemplified those illustrated below, those obtained by combining those illustrated below with a vinylene group, those obtained by combining two or more of those illustrated below, and the like.

Here, R represents a group selected from a hydrogen atom, an alkyl group having 1-20 carbon atoms, an aryl group having 6-60 carbon atoms, and a heterocyclic compound group having 4-60 carbon atoms, and Ar represents a hydrocarbon group having 6-60 carbon atoms.

[0033]



[0034]

This polymeric fluorescent substance may also be a random, block or graft copolymer, or a polymer having an intermediate structure thereof, for example, a random copolymer having block-like property. From the viewpoint for obtaining a polymeric fluorescent substance having high fluorescent quantum yield, random copolymers having block-like property and block or graft copolymers are more preferable than completely random copolymers. Further, copolymers may have a branched main

chain and have three or more terminals. Dendrimers are also included.

[0035]

Further, as the polymeric fluorescent substance, those emitting fluorescence in a solid state are suitably used, since the material utilizes light emission from a thin film.

[0036]

As good solvents for the polymeric fluorescent substance, there are exemplified chloroform, methylene chloride, dichloroethane, tetrahydrofuran, toluene, xylene, mesitylene, tetralin, decalin, n-butylbenzene and the like. The polymeric fluorescent substance can be usually dissolved in these solvents in an amount of 0.1 wt % or more, though the amount differs depending on the structure and molecular weight of the polymeric fluorescent substance.

[0037]

The polymeric fluorescent substance has a polystyrene-reduced number-average molecular weight of 10^3 to 10^5 , and the degree of polymerization thereof also changes depending on repeating structures and proportion thereof. From the standpoint of film forming property, generally the total amount of repeating structures is preferably from 20 to 10000, more preferably from 30 to 10000, particularly preferably from 50 to 5000.

When these polymeric fluorescent substances are used as

a light emitting material of a polymer LED, the purity thereof exerts an influence on light emitting property, therefore, it is preferable that a monomer before polymerization is purified by a method such as distillation, sublimation purification, re-crystallization and the like before being polymerized and further, it is preferable to conduct a purification treatment such as re-precipitation purification, chromatographic separation and the like after the synthesis.

[0038]

Next, the polymer LED of the present invention will be illustrated. The polymer LED of the present invention is a polymer LED comprising at least a light emitting layer between a pair of electrodes composed of an anode and a cathode at least one of which is transparent or semi-transparent wherein the light emitting layer contains a polymeric fluorescent substance of the present invention.

[0039]

As the polymer LED of the present invention, there are listed polymer LEDs having an electron transporting layer disposed between a cathode and a light emitting layer, polymer LEDs having a hole transporting layer disposed between an anode and a light emitting layer, polymer LEDs having an electron transporting layer disposed between a cathode and a light emitting layer and having a hole transporting layer disposed between an anode and a light emitting layer.

[0040]

For example, the following structures a) to d) are specifically exemplified.

a) anode/light emitting layer/cathode

b) anode/hole transporting layer/light emitting layer/cathode

c) anode/light emitting layer/electron transporting layer/cathode

d) anode/hole transporting layer/light emitting layer/electron transporting layer/cathode

(wherein, / indicates adjacent lamination of layers.

Hereinafter, the same)

Herein, the light emitting layer is a layer having function to emit a light, the hole transporting layer is a layer having function to transport a hole, and the electron transporting layer is a layer having function to transport an electron. Herein, the electron transporting layer and the hole transporting layer are generically called a charge transporting layer.

The light emitting layer, hole transporting layer and electron transporting layer may also each independently used in two or more layers.

[0041]

Of charge transporting layers disposed adjacent to an electrode, that having function to improve charge injecting

efficiency from the electrode and having effect to decrease driving voltage of an device are particularly called sometimes a charge injecting layer (hole injecting layer, electron injecting layer) in general.

[0042]

For enhancing adherence with an electrode and improving charge injection from an electrode, the above-described charge injecting layer or insulation layer having a thickness of 2 nm or less may also be provided adjacent to an electrode, and further, for enhancing adherence of the interface, preventing mixing and the like, a thin buffer layer may also be inserted into the interface of a charge transporting layer and light emitting layer.

[0043]

The order and number of layers laminated and the thickness of each layer can be appropriately applied while considering light emitting efficiency and life of the device.

[0044]

In the present invention, as the polymer LED having a charge injecting layer (electron injecting layer, hole injecting layer) provided, there are listed a polymer LED having a charge injecting layer provided adjacent to a cathode and a polymer LED having a charge injecting layer provided adjacent to an anode.

[0045]

For example, the following structures e) to p) are specifically exemplified.

e) anode/charge injecting layer/light emitting layer/cathode

f) anode/light emitting layer/charge injecting layer/cathode

g) anode/charge injecting layer/light emitting layer/charge injecting layer/cathode

h) anode/charge injecting layer/hole transporting layer/light emitting layer/cathode

i) anode/hole transporting layer/light emitting layer/charge injecting layer/cathode

j) anode/charge injecting layer/hole transporting layer/light emitting layer/charge injecting layer/cathode

k) anode/charge injecting layer/light emitting layer/electron transporting layer/cathode

l) anode/light emitting layer/electron transporting layer/charge injecting layer/cathode

m) anode/charge injecting layer/light emitting layer/electron transporting layer/charge injecting layer/cathode

n) anode/charge injecting layer/hole transporting layer/light emitting layer/electron transporting layer/cathode

o) anode/hole transporting layer/light emitting

layer/electron transporting layer/charge injecting
layer/cathode

p) anode/charge injecting layer/hole transporting
layer/light emitting layer/electron transporting layer/charge
injecting layer/cathode

As the specific examples of the charge injecting layer,
there are exemplified layers containing an conducting polymer,
layers which are disposed between an anode and a hole
transporting layer and contain a material having an ionization
potential between the ionization potential of an anode material
and the ionization potential of a hole transporting material
contained in the hole transporting layer, layers which are
disposed between a cathode and an electron transporting layer
and contain a material having an electron affinity between the
electron affinity of a cathode material and the electron affinity
of an electron transporting material contained in the electron
transporting layer, and the like.

[0046]

When the above-described charge injecting layer is a layer
containing an conducting polymer, the electric conductivity
of the conducting polymer is preferably 10^{-5} S/cm or more and
 10^3 S/cm or less, and for decreasing the leak current between
light emitting pixels, more preferably 10^{-5} S/cm or more and
 10^2 S/cm or less, further preferably 10^{-5} S/cm or more and 10^1
S/cm or less.

[0047]

Usually, to provide an electric conductivity of the conducting polymer of 10^{-5} S/cm or more and 10^3 S/cm or less, a suitable amount of ions are doped into the conducting polymer.

[0048]

Regarding the kind of an ion doped, an anion is used in a hole injecting layer and a cation is used in an electron injecting layer. As examples of the anion, a polystyrene sulfonate ion, alkylbenzene sulfonate ion, camphor sulfonate ion and the like are exemplified, and as examples of the cation, a lithium ion, sodium ion, potassium ion, tetrabutyl ammonium ion and the like are exemplified.

[0049]

The thickness of the charge injecting layer is for example, from 1 nm to 100 nm, preferably from 2 nm to 50 nm.

[0050]

Materials used in the charge injecting layer may properly be selected in view of relation with the materials of electrode and adjacent layers, and there are exemplified conducting polymers such as polyaniline and derivatives thereof, polythiophene and derivatives thereof, polypyrrole and derivatives thereof, poly(phenylene vinylene) and derivatives thereof, poly(thienylene vinylene) and derivatives thereof, polyquinoline and derivatives thereof, polyquinoxaline and derivatives thereof, polymers containing aromatic amine

structures in the main chain or the side chain, and the like, and metal phthalocyanine (copper phthalocyanine and the like), carbon and the like.

[0051]

The insulation layer having a thickness of 2 nm or less has function to make charge injection easy. As the material of the above-described insulation layer, metal fluoride, metal oxide, organic insulation materials and the like are listed. As the polymer LED having an insulation layer having a thickness of 2 nm or less, there are listed polymer LEDs having an insulation layer having a thickness of 2 nm or less provided adjacent to a cathode, and polymer LEDs having an insulation layer having a thickness of 2 nm or less provided adjacent to an anode.

[0052]

Specifically, there are listed the following structures q) to ab) for example.

q) anode/insulation layer having a thickness of 2 nm or less/light emitting layer/cathode

r) anode/light emitting layer/insulation layer having a thickness of 2 nm or less/cathode

s) anode/insulation layer having a thickness of 2 nm or less/light emitting layer/insulation layer having a thickness of 2 nm or less/cathode

t) anode/insulation layer having a thickness of 2 nm or less/hole transporting layer/light emitting layer/cathode

u) anode/hole transporting layer/light emitting layer/insulation layer having a thickness of 2 nm or less/cathode

v) anode/insulation layer having a thickness of 2 nm or less/hole transporting layer/light emitting layer/insulation layer having a thickness of 2 nm or less/cathode

w) anode/insulation layer having a thickness of 2 nm or less/light emitting layer/electron transporting layer/cathode

x) anode/light emitting layer/electron transporting layer/insulation layer having a thickness of 2 nm or less/cathode

y) anode/insulation layer having a thickness of 2 nm or less/light emitting layer/electron transporting layer/insulation layer having a thickness of 2 nm or less/cathode

z) anode/insulation layer having a thickness of 2 nm or less/hole transporting layer/light emitting layer/electron transporting layer/cathode

aa) anode/hole transporting layer/light emitting layer/electron transporting layer/insulation layer having a thickness of 2 nm or less/cathode

ab) anode/insulation layer having a thickness of 2 nm or less/hole transporting layer/light emitting layer/electron transporting layer/insulation layer having a thickness of 2 nm or less/cathode

In producing a polymer LED, when a film is formed from a solution by using such polymeric fluorescent substance soluble in an organic solvent, only required is removal of the solvent

by drying after coating of this solution, and even in the case of mixing of a charge transporting material and a light emitting material, the same method can be applied, causing an extreme advantage in production. As the film forming method from a solution, there can be used coating methods such as a spin coating method, casting method, micro gravure coating method, gravure coating method, bar coating method, roll coating method, wire bar coating method, dip coating method, spray coating method, screen printing method, flexo printing method, offset printing method, inkjet printing method and the like.

[0053]

Regarding the thickness of the light emitting layer, the optimum value differs depending on material used, and may properly be selected so that the driving voltage and the light emitting efficiency become optimum values, and for example, it is from 1 nm to 1 μ m, preferably from 2 nm to 500 nm, further preferably from 5 nm to 200 nm.

[0054]

In the polymer LED of the present invention, a light emitting material other than the above-mentioned polymeric fluorescent substances may be mixed in a light emitting layer. Further, in the polymer LED according to the instant application, a light emitting layer containing a light emitting material other than the above-mentioned polymeric fluorescent substance may be laminated with a light emitting layer containing the

above-mentioned polymeric fluorescent substance.

[0055]

As the light emitting material, known materials can be used. In a compound having lower molecular weight, there can be used, for example, naphthalene derivatives, anthracene or derivatives thereof, perylene or derivatives thereof; dyes such as polymethine dyes, xanthene dyes, coumarine dyes, cyanine dyes; metal complexes of 8-hydroxyquinoline or derivatives thereof, aromatic amine, tetraphenylcyclopentane or derivatives thereof, or tetraphenylbutadiene or derivatives thereof, and the like.

[0056]

Specifically, there can be used known compounds such as those described in JP-A Nos. 57-51781, 59-195393 and the like, for example.

[0057]

When the polymer LED of the present invention has a hole transporting layer, as the hole transporting materials used, there are exemplified polyvinylcarbazole or derivatives thereof, polysilane or derivatives thereof, polysiloxane derivatives having an aromatic amine in the side chain or the main chain, pyrazoline derivatives, arylamine derivatives, stilbene derivatives, triphenyldiamine derivatives, polyaniline or derivatives thereof, polythiophene or derivatives thereof, polypyrrole or derivatives thereof,

poly(p-phenylenevinylene) or derivatives thereof,
poly(2,5-thienylenevinylene) or derivatives thereof, or the
like.

[0058]

Specific examples of the hole transporting material include
those described in JP-A Nos. 63-70257, 63-175860, 2-135359,
2-135361, 2-209988, 3-37992 and 3-152184.

[0059]

Among them, as the hole transporting materials used in the
hole transporting layer, preferable are polymer hole
transporting materials such as polyvinylcarbazole or
derivatives thereof, polysilane or derivatives thereof,
polysiloxane derivatives having an aromatic amine compound
group in the side chain or the main chain, polyaniline or
derivatives thereof, polythiophene or derivatives thereof,
poly(p-phenylenevinylene) or derivatives thereof,
poly(2,5-thienylenevinylene) or derivatives thereof, or the
like, and further preferable are polyvinylcarbazole or
derivatives thereof, polysilane or derivatives thereof and
polysiloxane derivatives having an aromatic amine compound
group in the side chain or the main chain. In the case of a
hole transporting material having lower molecular weight, it
is preferably dispersed in a polymer binder for use.

[0060]

Polyvinylcarbazole or derivatives thereof are obtained,

for example, by cation polymerization or radical polymerization from a vinyl monomer.

[0061]

As the polysilane or derivatives thereof, there are exemplified compounds described in Chem. Rev., 89, 1359 (1989) and GB 2300196 published specification, and the like. For synthesis, methods described in them can be used, and a Kipping method can be suitably used particularly.

[0062]

As the polysiloxane or derivatives thereof, those having the structure of the above-described hole transporting material having lower molecular weight in the side chain or main chain, since the siloxane skeleton structure has poor hole transporting property. Particularly, there are exemplified those having an aromatic amine having hole transporting property in the side chain or main chain.

[0063]

The method for forming a hole transporting layer is not restricted, and in the case of a hole transporting layer having lower molecular weight, a method in which the layer is formed from a mixed solution with a polymer binder is exemplified. In the case of a polymer hole transporting material, a method in which the layer is formed from a solution is exemplified.

[0064]

The solvent used for the film forming from a solution is

not particularly restricted providing it can dissolve a hole transporting material. As the solvent, there are exemplified chlorine solvents such as chloroform, methylene chloride, dichloroethane and the like, ether solvents such as tetrahydrofuran and the like, aromatic hydrocarbon solvents such as toluene, xylene and the like, ketone solvents such as acetone, methyl ethyl ketone and the like, and ester solvents such as ethyl acetate, butyl acetate, ethylcellosolve acetate and the like.

[0065]

As the film forming method from a solution, there can be used coating methods such as a spin coating method, casting method, micro gravure coating method, gravure coating method, bar coating method, roll coating method, wire bar coating method, dip coating method, spray coating method, screen printing method, flexo printing method, offset printing method, inkjet printing method and the like, from a solution.

[0066]

The polymer binder mixed is preferably that does not disturb charge transport extremely, and that does not have strong absorption of a visible light is suitably used. As such polymer binder, polycarbonate, polyacrylate, poly(methyl acrylate), poly(methyl methacrylate), polystyrene, poly(vinyl chloride), polysiloxane and the like are exemplified.

[0067]

Regarding the thickness of the hole transporting layer, the optimum value differs depending on material used, and may properly be selected so that the driving voltage and the light emitting efficiency become optimum values, and at least a thickness at which no pin hole is produced is necessary, and too large thickness is not preferable since the driving voltage of the device increases. Therefore, the thickness of the hole transporting layer is, for example, from 1 nm to 1 μ m, preferably from 2 nm to 500 nm, further preferably from 5 nm to 200 nm.

[0068]

When the polymer LED of the present invention has an electron transporting layer, known compounds are used as the electron transporting materials, and there are exemplified oxadiazole derivatives, anthraquinonedimethane or derivatives thereof, benzoguinone or derivatives thereof, naphthoquinone or derivatives thereof, anthraquinone or derivatives thereof, tetracyanoanthraquinodimethane or derivatives thereof, fluorenone derivatives, diphenyldicyanoethylene or derivatives thereof, diphenoguinone derivatives, or metal complexes of 8-hydroxyquinoline or derivatives thereof, polyquinoline and derivatives thereof, polyquinoxaline and derivatives thereof, polyfluorene or derivatives thereof, and the like.

[0069]

Specifically, there are exemplified those described in JP-A

Nos. 63-70257, 63-175860, 2-135359, 2-135361, 2-209988, 3-37992 and 3-152184.

[0070]

Among them, oxadiazole derivatives, benzoquinone or derivatives thereof, anthraquinone or derivatives thereof, or metal complexes of 8-hydroxyquinoline or derivatives thereof, polyquinoline and derivatives thereof, polyquinoxaline and derivatives thereof, polyfluorene or derivatives thereof are preferable, and

2-(4-biphenyl)-5-(4-t-butylphenyl)-1,3,4-oxadiazole, benzoquinone, anthraquinone, tris(8-quinolinol)aluminum and polyquinoline are further preferable.

[0071]

The method for forming the electron transporting layer is not particularly restricted, and in the case of an electron transporting material having lower molecular weight, a vapor deposition method from a powder, or a method of film-forming from a solution or melted state is exemplified, and in the case of a polymer electron transporting material, a method of film-forming from a solution or melted state is exemplified, respectively. When film-forming is conducted from a solution or melted state, a polymer binder may be used together.

[0072]

The solvent used in the film-forming from a solution is not particularly restricted provided it can dissolve electron

transporting materials and/or polymer binders. As the solvent, there are exemplified chlorine solvents such as chloroform, methylene chloride, dichloroethane and the like, ether solvents such as tetrahydrofuran and the like, aromatic hydrocarbon solvents such as toluene, xylene and the like, ketone solvents such as acetone, methyl ethyl ketone and the like, and ester solvents such as ethyl acetate, butyl acetate, ethyl cellosolve acetate and the like.

[0073]

As the film-forming method from a solution or melted state, there can be used coating methods such as a spin coating method, casting method, micro gravure coating method, gravure coating method, bar coating method, roll coating method, wire bar coating method, dip coating method, spray coating method, screen printing method, flexo printing method, offset printing method, inkjet printing method and the like.

[0074]

The polymer binder to be mixed is preferably that which does not extremely disturb a charge transport property, and that does not have strong absorption of a visible light is suitably used. As such polymer binder, poly(N-vinylcarbazole), polyaniline or derivatives thereof, polythiophene or derivatives thereof, poly(p-phenylene vinylene) or derivatives thereof, poly(2,5-thienylene vinylene) or derivatives thereof, polycarbonate, polyacrylate, poly(methyl acrylate),

poly(methyl methacrylate), polystyrene, poly(vinyl chloride), polysiloxane and the like are exemplified.

[0075]

Regarding the thickness of the electron transporting layer, the optimum value differs depending on material used, and may properly be selected so that the driving voltage and the light emitting efficiency become optimum values, and at least a thickness at which no pin hole is produced is necessary, and too large thickness is not preferable since the driving voltage of the device increases. Therefore, the thickness of the electron transporting layer is, for example, from 1 nm to 1 μ m, preferably from 2 nm to 500 nm, further preferably from 5 nm to 200 nm.

[0076]

The substrate forming the polymer LED of the present invention may preferably be that does not change in forming an electrode and layers of organic materials, and there are exemplified glass, plastics, polymer film, silicon substrates and the like. In the case of a opaque substrate, it is preferable that the opposite electrode is transparent or semitransparent.

[0077]

In the present invention, it is preferable that an anode is transparent or semitransparent, and as the material of this anode, electron conductive metal oxide films, semitransparent metal thin films and the like are used. Specifically, there

are used indium oxide, zinc oxide, tin oxide, and films (NESA and the like) fabricated by using an electron conductive glass composed of indium·tin·oxide (ITO), indium·zinc·oxide and the like, which are metal oxide complexes, and gold, platinum, silver, copper and the like are used, and among them, ITO, indium·zinc·oxide, tin oxide are preferable. As the fabricating method, a vacuum vapor deposition method, sputtering method, ion plating method, plating method and the like are used. As the anode, there may also be used organic transparent conducting films such as polyaniline or derivatives thereof, polythiophene or derivatives thereof and the like.

[0078]

The thickness of the anode can be appropriately selected while considering transmission of a light and electric conductivity, and for example, from 10 nm to 10 μ m, preferably from 20 nm to 1 μ m, further preferably from 50 nm to 500 nm.

[0079]

Further, for easy charge injection, there may be provided on the anode a layer comprising a phthalocyanine derivative conducting polymers, carbon and the like, or a layer having an average film thickness of 2 nm or less comprising a metal oxide, metal fluoride, organic insulating material and the like.

[0080]

As the material of a cathode used in the polymer LED of the present invention, that having lower work function is

preferable. For example, there are used metals such as lithium, sodium, potassium, rubidium, cesium, beryllium, magnesium, calcium, strontium, barium, aluminum, scandium, vanadium, zinc, yttrium, indium, cerium, samarium, europium, terbium, ytterbium and the like, or alloys comprising two or more of them, or alloys comprising one or more of them with one or more of gold, silver, platinum, copper, manganese, titanium, cobalt, nickel, tungsten and tin, graphite or graphite intercalation compounds and the like. Examples of alloys include a magnesium-silver alloy, magnesium-indium alloy, magnesium-aluminum alloy, indium-silver alloy, lithium-aluminum alloy, lithium-magnesium alloy, lithium-indium alloy, calcium-aluminum alloy and the like. The cathode may be formed into a laminated structure of two or more layers.

[0081]

The film thickness of a cathode can be appropriately selected in view of electric conductivity and durability, and for example, it is from 10 nm to 10 μ m, preferably from 20 nm to 1 μ m, further preferably from 50 nm to 500 nm.

[0082]

As the method for fabricating a cathode, there are used a vacuum vapor deposition method, sputtering method, lamination method in which a metal thin film is adhered under heat and pressure, and the like. Further, there may also be provided,

between a cathode and an organic layer, a layer comprising an conducting polymer, or a layer having an average film thickness of 2 nm or less comprising a metal oxide, metal fluoride, organic insulation material and the like, and after fabrication of the cathode, a protective layer may also be provided which protects the polymer LED. For stable use of the polymer LED for a long period of time, it is preferable to provide a protective layer and/or protective cover for protection of the device in order to prevent it from outside damage.

[0083]

As the protective layer, there can be used a polymer compound, metal oxide, metal fluoride, metal borate and the like. As the protective cover, there can be used a glass plate, a plastic plate the surface of which has been subjected to lower-water-permeation treatment, and the like, and there is suitably used a method in which the cover is pasted with an device substrate by a thermosetting resin or light-curing resin for sealing. If space is maintained using a spacer, it is easy to prevent an device from being injured. If an inner gas such as nitrogen and argon is sealed in this space, it is possible to prevent oxidation of a cathode, and further, by placing a desiccant such as barium oxide and the like in the above-described space, it is easy to suppress the damage of an device by moisture adhered in the production process. Among them, any one means or more are preferably adopted.

[0084]

For obtaining light emission in plane form using the polymer LED of the present invention, an anode and a cathode in the plane form may properly be placed so that they are laminated each other. Further, for obtaining light emission in pattern form, there are a method in which a mask with a window in pattern form is placed on the above-described plane light emitting device, a method in which an organic layer in non-light emission part is formed to obtain extremely large thickness providing substantial non-light emission, and a method in which any one of an anode or a cathode, or both of them are formed in the pattern. By forming a pattern by any of these methods and by placing some electrodes so that independent on/off is possible, there is obtained a display device of segment type which can display digits, letters, simple marks and the like. Further, for forming a dot matrix device, it may be advantageous that anodes and cathodes are made in the form of stripes and placed so that they cross at right angles. By a method in which a plurality of kinds of polymeric fluorescent substances emitting different colors of lights are placed separately or a method in which a color filter or luminescence converting filter is used, area color displays and multi color displays are obtained. A dot matrix display can be driven by passive driving, or by active driving combined with TFT and the like. These display devices can be used as a display of a computer, television,

portable terminal, portable telephone, car navigation, view finder of a video camera, and the like.

[0085]

Further, the above-described light emitting device in plane form is a thin self-light-emitting one, and can be suitably used as a flat light source for back-light of a liquid crystal display, or as a flat light source for illumination. Further, if a flexible plate is used, it can also be used as a curved light source or a display.

[0086]

[EXAMPLES]

The following examples further illustrate the present invention in detail but do not limit the scope thereof.

Herein, regarding the number average molecular weight, a polystyrene reduced number-average molecular weight was measured by gel permeation chromatography (GPC) using chloroform as a solvent.

[0087]

Example 1

<Synthesis of 2,6-dibromo-1,5-dihexyloxynaphthalene>

Under an inert atmosphere, sodium methoxide (2.76g, 40.6mmol) and 2,6-dibromo-1,5-dihydroxynaphthalene (5g, 15.7mmol) were dissolved in ethanol (60ml). Under reflux, ethanol solution (10ml) of hexylbromide (6.7g, 40.6mmol) was added dropwise in 10 minutes. It was refluxed for 5 hours and then

left for cooling. The reaction mixture was added to 1N sodium-hydroxide aqueous solution, and the depositing precipitate was filtrated. The precipitate was washed with methylene chloride, and the washed solution was concentrated under a reduced pressure to obtain a crude product. The desired product was obtained after purifying by silica gel chromatography (toluene:hexane =4:1).

The amount was 3.72g, and the yield was 48%.

[0088]

<Synthesis of 9,9-dioctylfluorene-2,7-bis(ethylene boronate)>

2, 7-di bromo fluorene (25g, 77mmol), octylbromide (44.7g, 0.596 mols), sodium hydroxide (37.5g, 0.937 mols), and tetrabutyl ammonium bromide (0.5g, 1.55mmol) were dissolved in dimethyl sulfoxide (75ml)-water (37.5ml) mixed solvent. It was kept warm at 80 °C for 6 hours. After cooling, toluene (100ml) and water (100ml) were added, and the organic layer was partitioned. The organic layer is washed with water, 3% hydrochloric acid, and water, and then dehydrated with anhydrous sodium sulfate. The solvent was distilled off under reduced pressure and the crude product was purified by silica-gel chromatography, and 2,7-dibromo-9,9-dioctylfluorene was obtained. (Amount:26.85g, yield:79%)

The resultant 2,7-dibromo-9,9-dioctylfluorene (24.7g,

22.8mmol) was dissolved in tetrahydrofuran under an inert atmosphere, and cooled to -70°C or less. To this, 1.6M of n-butyllithium (61.9ml) was added dropwise in 40 minutes. After 2 hours stirring, trimethoxyborane (14.0g, 135mmol) was added dropwise in 5 minutes. After raising the temperature to a room temperature, the mixture was added into 5% sulfuric acid, and the organic layer was partitioned. The aqueous layer was extracted with ethylacetate, and the organic layers was collected and washed with water. The organic layer was dried by molecular sieves and the solvent was distilled off under reduced pressure. The residue was suspended in hexane, filtrated off the insoluble material, and a crude product of 9,9-dioctylfluorene-2,7-di-boronic acid was obtained (12.56g, 26.3mmol).

The crude product was dissolved in 630ml of toluene together with ethylene glycol (33.85g, 0.545 mols). 500ml of the toluene was distilled off at 115°C , and the same amount of toluene was added. The distillation-addition was conducted repeatedly two times, left for cooling, and then the organic layer was washed with water, and dehydrated with anhydrous sodium sulfate. The solvent was distilled off under reduced pressure and the crude product was purified by silica-gel chromatography (toluene:ethylacetate=5:1), and 9,9-dioctylfluorene-2,7-bis(ethylene boronate). The amount was 6.65g, and the yield was 54%.

[0089]

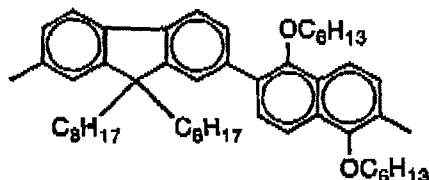
<Synthesis of

poly(9,9-dioctylfluorene-1,5-dihexyloxy-2,6-naphthalene)>

Under an inert atmosphere,

9,9-dioctylfluorene-2,7-bis(ethylene boronate) (305 mg, 0.574 mmol), 2,6-dibromo-1,5-dihexyloxynaphthalene (266 mg, 0.549 mmol) and aliquat® 336 (tricaprylylmethylammonium chloride, manufactured by Aldrich, 200 mg, 0.497 mmol) were dissolved in toluene (10 ml) and to this was added 10 ml of an aqueous solution of potassium carbonate (225 mg, 1.49 mmol). Further, tetrakis(triphenylphosphine)palladium (19 mg, 0.015 mmol) was added, and the mixture was heated under reflux for 20 hours. After cooling, the solution was separated, and the organic layer was washed with water. This organic layer was dropped into methanol, and the deposited precipitate was filtrated off to obtain Polymeric fluorescent substance 1'. The yield was 190 mg. By NMR, it was confirmed that the obtained polymer has a following repeating unit expected from the charged monomer.

[0090]



[0091]

Polymeric fluorescent substance 1' had a polystyrene-reduced number-average molecular weight of 1.9

$\times 10^4$. Polymeric fluorescent substance 1 could be dissolved in a solvent such as toluene, chloroform and the like.

[0092]

<Evaluation of fluorescent property>

A 0.4 wt% chloroform solution of Polymeric fluorescent substance 1 was spin-coated on quartz, to form a thin film of Polymeric fluorescent substance 1'. The ultraviolet visible absorption spectrum and fluorescent spectrum of this thin film were measured by using a ultraviolet visible absorption spectrophotometer (UV3500 manufactured by Hitachi, Ltd.) and a fluorescent spectrophotometer (850 manufactured by Hitachi, Ltd.), respectively. For calculation of fluorescent strength, a fluorescent spectrum excited at 350 nm was used. The area of fluorescent spectra plotted against wave-number on the abscissa was divided by the absorption at 350 nm, to obtain a relative value of the fluorescent strength.

Polymeric fluorescent substance 1' has a fluorescent peak wave-length of 484 nm, and revealed a relative value of the fluorescent strength of 2.0.

[0093]

<Production and evaluation of the device>

On a glass substrate on which an ITO film had been made at a thickness of 150 nm according to a sputtering method, a film having a thickness of 50 nm was formed using a solution (Baytron, manufactured by Bayer) of

poly(ethylenedioxythiophene)/polystyrenesulfonic acid by spin coating, and the film was dried at 120°C for 10 minutes on a hot plate. Then, a film having a thickness of about 70 nm was formed using a 1.5 wt% toluene solution of Polymeric fluorescent substance 1' by spin coating. Further, this film was dried at 80°C for 1 hour under reduced pressure, then, lithium fluoride was vapor-deposited at 0.4 nm as a cathode buffer layer, calcium was vapor-deposited at 25 nm and aluminum was vapor-deposited at 40 nm as a cathode, to produce a polymer LED. In any vapor deposition, the degree of vacuum was 1 to 8×10^{-6} Torr. Voltage was applied on the resulted device, to give EL light emission from Polymeric fluorescent substance 1'. The strength of EL light emission was approximately in proportion to the current density. Maximum light emitting efficiency was about 1.4 cd/A.

[0094]

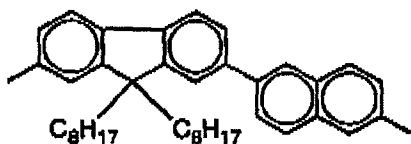
Comparative Example 1

<Synthesis of poly(9,9-dioctylfluorene-1,5-naphthalene)>

Under an inert atmosphere, 9,9-dioctylfluorene-2,7-bis(ethylene boronate) (305 mg, 0.574 mmol), 2,6-dibromonaphthalene (142 mg, 0.549 mmol) and aliquat® 336 (tricaprylylmethylammonium chloride, manufactured by Aldrich, 200 mg, 0.497 mmol) were dissolved in toluene (10 ml) and to this was added 10 ml of an aqueous solution of potassium carbonate (225 mg, 1.49 mmol). Further,

tetrakis(triphenylphosphine)palladium (19 mg, 0.015 mmol) was added, and the mixture was heated under reflux for 20 hours. After cooling, the solution was separated, and the organic layer was washed with water. This organic layer was dropped into methanol, and the deposited precipitate was filtrated off to obtain Polymeric fluorescent substance 2'. The yield was 99 mg. By NMR, it was confirmed that the obtained polymer has a following repeating unit expected from the charged monomer.

[0095]



[0096]

Polymeric fluorescent substance 2' had a polystyrene-reduced number-average molecular weight of 2.0×10^4 . Polymeric fluorescent substance 2' could be dissolved in a solvent such as toluene, chloroform and the like.

<Evaluation of fluorescent property>

The relative value of the fluorescent strength of polymeric fluorescent substance 2' was obtained as the same manner with Example 1.

Polymeric fluorescent substance 2' has a fluorescent peak wave-length of 428 nm, and a relative value of the fluorescent strength of 0.42.

[0097]

<Production and evaluation of the device>

A polymer LED was produced in the same manner with Example 1 except that polymeric fluorescent substance 2' was used instead of polymeric fluorescent substance 1'. Voltage was applied on the resulted device, to give EL light emission from Polymeric fluorescent substance 2'. The strength of EL light emission was approximately in proportion to the current density. Maximum light emitting efficiency was about 0.1 cd/A.

[0098]

Example 2

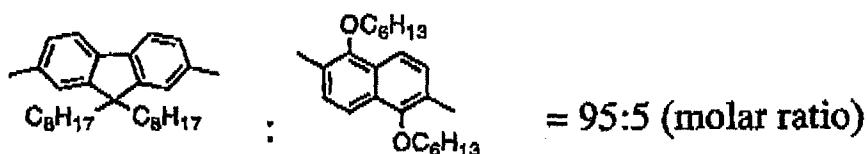
<Synthesis of

poly(9,9-dioctylfluorene-co-1,5-dihexyloxy-2,6-naphthalene)
>>

Under an inert atmosphere,
9,9-dioctylfluorene-2,7-bis(ethylene boronate) (305 mg, 0.574 mmol), 2,7-dibromo-9,9-dioctylnaphthalene (270 mg, 0.492 mmol), 2,6-dibromo-1,5-dihexyloxynaphthalene (26.6 mg, 0.0549 mmol), and aliquat® 336 (tricaprylylmethylammonium chloride, manufactured by Aldrich, 200 mg, 0.549 mmol) were dissolved in toluene (10 ml) and to this was added 10 ml of an aqueous solution of potassium carbonate (238 mg, 1.72 mmol). Further, tetrakis(triphenylphosphine)palladium (1.27 mg, 0.0011 mmol) was added, and the mixture was heated under reflux for 10 hours. After cooling, the solution was separated, and the organic layer

was washed with water. This organic layer was dropped into methanol, and the deposited precipitate was filtrated off to obtain Polymeric fluorescent substance 3'. The yield was 280 mg. By NMR, it was confirmed that the obtained polymer has a following repeating unit expected from the charged monomer.

[0099]



[0100]

Polymeric fluorescent substance 3' had a polystyrene-reduced number-average molecular weight of 3.5×10^4 . Polymeric fluorescent substance 3' could be dissolved in a solvent such as toluene, and chloroform.

<Evaluation of fluorescent property>

The relative value of the fluorescent strength of polymeric fluorescent substance 3' was obtained as the same manner with Example 1.

Polymeric fluorescent substance 3' has a fluorescent peak wave-length of 426 nm, and a relative value of the fluorescent strength of 4.98.

[0101]

[Effect of the Invention]

The polymeric fluorescent substance of the present invention is a polymeric fluorescent substance comprising a fluorene and naphthalene, and shows strong fluorescence, and can be suitably used as a polymer LED or a pigment for laser. The polymer LED using this polymeric fluorescent substance is a polymer LED of high performance which can be driven at lower voltage with high efficiency. Therefore, this polymer LED can be preferably used as a back light of a liquid crystal display, a light source in the form of curved surface or flat surface for illumination, or a display device of segment type, and in apparatuses such as a flat panel display of dot matrix, and the like.